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(54) **TETRAFLUOROETHANE COMPOSITION FOR A REGRIGERATOR**

TETRAFLUORÄTHANGEMISCH FÜR EINEN KÜHLSCHRANK

COMPOSE A BASE DE TETRAFLUOROETHANE POUR REFRIGERATEURS

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(56) References cited:
EP-A- 0 030 127
EP-A- 0 048 281
EP-A- 0 062 516
DE-A- 3 202 478
DE-A- 3 235 561
DE-A- 3 514 108
DE-A- 3 543 171
DE-C- 3 003 471
DE-C- 3 524 737
GB-B- 1 379 956

- **Patent Abstracts of Japan, Vol 7, No 11, C145, abstract of JP 57-168979, publ 1982-10-18**
- **Patent Abstracts of Japan, Vol 9, No 166, C290, abstract of JP 60- 40185, publ 1985-03-02**
- **Patent Abstracts of Japan, Vol 7, No 147, C173, abstract of JP 58- 61173, publ 1983-04-12**
- **Patent Abstracts of Japan, Vol 8, No 41, C211, abstract of JP 58-201878, publ 1983-11-24**

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TECHNICAL FIELD

The present invention relates to a composition for a refrigerator comprising a tetrafluoroethane and a polyether which is compatible at any optional ratio with a tetrafluoroethane, preferably 1,1,1,2-tetrafluoroethane (R-134a), as a cooling medium at a temperature of from -20°C or lower to +40°C or higher and which has a low hygroscopic property.

R-12 (dichlorodifluoromethane) is used as an excellent cooling medium in a refrigerating cycle of e.g refrigerators or car air conditioners. However, R-12 is likely to destroy the ozone layer in the stratosphere and adversely affect the living bodies. Therefore, a study for a substitute material is being made. As a substitute for R-12, R-134a is considered to be most prospective. However, a naphthene mineral oil and a paraffin mineral oil which are refrigerator oils commonly used for R-12, are incompatible with R-134a. Therefore, such a naphthene mineral oil or paraffin mineral oil can not be used as a refrigerator oil for R-134a. Polyether oils having the structures as identified in Table 1 are known as substances relatively well compatible with R-134a.

The polyether oil (a) is disclosed, for example, in Dupont Research Disclosure (17483, Oct., 1978). The polyether oil (b) is disclosed, for example, in US Patent 4,755,316.

However, the polyether oils as identified in Table 1 had the following problems.

(1) Compatibility with R-134a is not adequate. In order to provide a lubricating property as the most important role of the freezer oil, it is essential that the oil is compatible with R-134a and capable of being circulated in the system together with R-134a. With respect to the freezer oils (a) and (b), the upper critical solution temperatures (see the footnote of Table 1) are as shown in Table 1 in the case where the kinematic viscosity at 40°C is 100×10^{-6} m^2/s (100 cSt). The compatibility can hardly be regarded as adequate.

(2) Hygroscopicity is high. The freezer oils (a) and (b) are highly hygroscopic and apt to absorb moisture. Inclusion of moisture brings about adverse affects such as a deterioration of insulation resistance and an increase of corrosiveness to metal.

Table 1:
Conventional polyether oils and their upper critical solution temperatures

No.	Structure	Upper critical solution temperature* of a product with 100×10^{-6} m^2/s (100 cSt) at 40°C
(a)	$C_4H_9-O(C_3H_6O)_nH$	12°C
(b)	$C3H6\begin{cases} O-(C_3H_6O)_n-H \\ O-(C_3H_6O)_n-H \end{cases}$	40°C

(*) Upper critical temperature: The oil and R-134a are mixed in a weight ratio of 15:85 and sealed. The temperature is gradually raised, and the temperature at which turbidity or phase separation has started, is taken as the upper critical solution temperature. The better the compatibility, the higher the upper critical solution temperature.

To solve the above problems, the present inventors have presumed that the hygroscopicity of the polyether oils is attributable to the terminal hydroxyl groups. Therefore, by using polyethers having from 1 to 3 terminal hydroxyl groups, all or a part of the terminal hydroxyl groups of such polyethers have been acylated or alkylated, and evaluation of such acylated or alkylated compounds for usefulness as freezer oils for R-134a has been conducted. As a result, it has been found that not only the hygroscopicity but also the compatibility with R-134a and the viscosity indexes have been improved. The present invention has been accomplished on the basis of this discovery.

The present invention provides a refrigeration composition, with functions of prevention of friction, abrasion and seizing of sliding portions, which comprises a tetrafluoroethane and at least one polyether selected from the group consisting of:

$$R^2-O-(R^1O)_{\ell}-R^3 \qquad (1)$$

$$X^1\begin{array}{l} \diagup O\text{-}(R^1O)_{\ell}\text{-}R^4 \\ \diagdown O\text{-}(R^1O)_m\text{-}R^5 \end{array} \qquad (2)$$

$$X^1\begin{array}{l} \diagup O\text{-}(R^1O)_{\ell}\text{-}R^6 \\ \text{-}O\text{-}(R^1O)_m\text{-}R^7 \\ \diagdown O\text{-}(R^1O)_n\text{-}R^8 \end{array} \qquad \cdots (3)$$

wherein R^1 is an alkylene group, each of R^2, R^3, R^4, R^5, R^6, R^7 and R^8 which may be the same or different is a hydrogen atom, an alkyl group, a hydroxyalkylgroup, an aralkyl group, an aryl group, an acyl group, a glycidyl group, $-SO_2R^9$,

$$\begin{array}{c} -\underset{\displaystyle \overset{\|}{O}}{C}NHR^{10}, \end{array}$$

$$-\underset{\displaystyle \overset{\|}{O}}{C}OR^{11} \quad \text{or} \quad -Y^1\text{-}(OR^1)_p\text{-}OR^{12}$$

wherein R^1 is as defined above, each of R^9, R^{10}, R^{11} and R^{12} is an alkyl group, a hydroxyalkyl group, an aralkyl group or an aryl group, wherein all or a part of hydrogen atoms of said alkyl, aralkyl or aryl groups may be substituted by halogen atoms and Y^1 is a residue of a dicarboxylic compound having at least 3 carbon atoms, provided that at least one of R^2 and R^3 and at least one of R^4 and R^5 are not hydrogen atoms, and when R^2 is a hydrogen atom, an alkyl group for R^3 has 1 or 2 carbon atoms, and when R^3 is a hydrogen atom, an alkyl group for R^2 has 1 or 2 carbon atoms, ℓ, m, n and p which may be the same or different are integers which bring the kinematic viscosity of the compounds of the formulas (1) to (3) to a level of from 5×10^{-6} to 300×10^{-6} m^2/s (5 to 300 cSt) at 40°C, X^1 is a residue obtained by removing hydroxyl groups from a dihydroxy compound or a dicarboxylic compound, and X^2 is a residue obtained by removing hydroxyl groups from a trihydroxy compound or a tricarboxylic compound.

Now, the present invention will be described in detail with reference to the preferred embodiments.

In the above definitions, the alkyl group includes, for example, a methyl group, an ethyl group, a propyl group, a butyl group, a 2-ethylhexyl group and a nonyl group. The aralkyl group includes, for example, a benzyl group, a phenylethyl group and a methylbenzyl group. The aryl group includes, for example, a phenyl group and a tolyl group. All or a part of hydrogen atoms of these hydrocarbon groups may be substituted by halogen atoms such as fluorine atoms or chlorine atoms. Further, the alkyl group may be a hydroxyalkyl group such as a hydroxymethyl group, a hydroxyethyl group or a hydroxybutyl group.

The acyl group may be an acyl group of the formula

$$-\underset{\displaystyle \overset{\|}{O}}{C}-A,$$

wherein A is the above-mentioned alkyl, aralkyl or aryl group.

The above-mentioned alkyl, aralkyl or aryl group may be employed also for R^9, R^{10}, R^{11} and R^{12} in the above-mentioned radicals of the formulas $-SO_2R^9$,

$$-\underset{\underset{O}{\|}}{C}NHR^{10},$$

$$-\underset{\underset{O}{\|}}{C}OR^{11} \text{ or } -Y^1\!\!-\!\!(OR^1)_p\!\!-\!\!OR^{12}.$$

Y^1 is a residue obtained by removing both hydroxyl groups from a dicarboxylic compound having at least 3 carbon atoms. The dicarboxylic compound includes, for example, aliphatic dicarboxylic acids such as malonic acid, succinic acid, glutaric acid, adipic acid, sebacic acid, suberic acid, methyl succinic acid, methyl adipic acid, maleic acid, fumaric acid and itaconic acid; aromatic dicarboxylic acids such as phthalic acid, diphenyl dicarboxylic acid and diphenyl methane dicarboxylic acid; hydrogenated products of the above aromatic dicarboxylic acids, such as alicyclic dicarboxylic acids; and dicarboxylic acids prepared by introducing carboxyl groups to both terminals of polyalkylene glycols having a molecular weight of from 50 to 1,000.

X^1 in the formula (2) is preferably a residue obtained by removing hydroxyl groups from a dihydroxy compound, such as an ethylene glycol residue or a propylene glycol residue, or a residue obtained by removing hydroxyl groups from the same dicarboxylic compound as mentioned above for the definition of Y^1.

X^2 in the formula (3) is preferably a residue obtained by removing hydroxyl groups from a trihydroxy compound, such as a glycerol residue or a trimethylol propane residue, or a residue obtained by removing hydroxyl groups from a tricarboxylic compound such as trimellitic acid or trimesic acid.

R^1 in the formulas (1) to (3) and in the radical of the formula

$$-Y^1\!\!-\!\!(OR^1)_p\!\!-\!\!OR^{12}$$

is an alkylene group such as an ethylene group, a propylene group, a butylene group or a tetramethylene group. These alkylene groups may be present alone or in combination in the form of a random or block state. In the case of the combination, the main component is preferably a propylene group. R^1 in the formulas (2) and (3) may be the same or different. For the preparation of the compounds of the formulas (1), (2) and (3), the corresponding initiators are

$$R^2\text{-}OH,\quad X^1\begin{matrix}\diagup OH\\ \diagdown OH\end{matrix}\quad \text{and}\quad X^2\begin{matrix}\diagup OH\\ -OH\\ \diagdown OH\end{matrix},$$

respectively, and the numbers of active hydrogen groups thereof are 1, 2 and 3, respectively. If it is attempted to obtain a compound having a kinematic viscosity within range of from 12×10^{-6} to 300×10^{-6} m^2/s (12 cSt to 200 cSt) (40°C) which is common to freezer oils for car air conditioners or refrigerators, by using an initiator having 4 or more active hydrogen groups, the numbers for ℓ, m and n, i.e. the addition molar numbers of alkylene oxides, tend to be too small, whereby the lubricating property will be low, such being undesirable.

The compounds of the formulas (1) to (3) are desired to have a kinematic viscosity of from 5×10^{-6} to 300×10^{-6} m^2/s (5 to 300 cSt) (40°C), preferably from 12×10^{-6} to 300×10^{-6} m^2/s (12 to 200 cSt) (40°C), so that they provide adequate functions as freezer oils such as the functions for preventing friction, abrasion and seizing of sliding portions of e.g. compressors. Accordingly, it is desirable that the molecular weights of the compounds of the formulas (1) to (3) or the values for ℓ, m and n and the value for p in the formula

$$-Y^1\!\!-\!\!(OR^1)_p\!\!-\!\!OR^{12}$$

are selected so as to bring the kinematic viscosity within the above-mentioned range. The values for ℓ, m, n and p are from 6 to 30, and they may be the same or different.

The weight ratio of the compounds of the formulas (1) to (3) to R-134a is usually from 1/99 to 99/1, preferably from 5/95 to 60/40. R-134a may contain a small amount of 1,1,2,2-tetrafluoroethane (R-134). The compounds of the formulas (1) to (3) may be used alone or in combination as their mixtures.

The composition of the present invention is particularly effective when applied to a refrigerating cycle intended for freezing, for refrigerating and for air conditioning. However, it is also useful for other various heat recovery technologies such as a Rankine cycle.

The composition of the present invention has excellent heat stability and requires no stabilizer under a usual application condition. However, if an improvement of the heat stability for use under a severe condition is desired, a small amount of a stabilizer including a phosphite compound such as dimethyl phosphite, diisopropyl phosphite or diphenyl phosphite, a phosphine sulfide compound such as triphenoxy phosphine sulfide or trimethyl phosphine sulfide, and other glycidyl ethers, may be added. Further, the compounds of the formulas (1) to (3) of the present invention may be used in combination with conventional oils such as a naphthene mineral oil, a paraffin mineral oil, an alkylbenzene synthetic oil, a poly-α-olefin synthetic oil, a fluorine type lubricating oil such as a perfluoropolyether oil or a fluorine-containing silicone oil, or polyether oils other than the polyether oils of the present invention.

Further, various additives including a phenol type or amine type antioxidant, a sulfur or phosphorus type high pressure additive, a silicone type anti-foaming agent or a metal inactivating agent such as benzotriazole, may be added to the composition of the present invention.

It is believed that in the present invention, the hydrophilicity is lowered by the modification such as acylation or alkylation of the terminal hydroxyl groups and the hygroscopicity oil is thereby lowered. The mechanism for the compatibility of the oils of the present invention with tetrafluoroethane as a cooling medium, is not clearly understood. However, a certain interaction between tetrafluoroethane and the carbonyl group of the ester bond or the like, is related thereto.

Now, the present invention will be described in further detail with reference to Examples. However, it should be understood that the present invention is by no means restricted by such specific Examples. EXAMPLES 1-1 TO 1-5 AND COMPARATIVE EXAMPLES 1-1 TO 1-5

The structures of the oils used in Examples 1-1 to 1-5 and Comparative Examples 1-1 to 1-5 and the test results for their compatibility with R-134a, hygroscopicity and kinematic viscosities at 40°C, are shown in Table 2.

Method for testing hygroscopicity:

Into a Petri dish having a diameter of 150 mm, 15 g of an oil having a water content of not higher than 0.03% is introduced. The Petri dish is left open in a constant humidity and temperature room at a temperature of 20°C under a humidity of 50%. The weight increase is calculated by the following equation in which Y is the weight (g) of the oil upon expiration of 30 hours.

$$\text{Weight increase} = \frac{Y - 15}{15} \times 100\ (\%)$$

Table 2

No.	Polyether	Upper critical solution temperature (°C) (Compatibility with R-134a)	Weight increase (%) (Hygroscopicity)	Kinematic viscosity at 40°C (cSt) x 10^{-6} m^2/s
Example 1-1	C_3H_6 $\begin{cases} O(C_3H_6O)_{6.7}COCH_3 \\ O(C_3H_6O)_{6.7}COCH_3 \end{cases}$	78	0.7	55.4
Comparative Example 1-1	C_3H_6 $\begin{cases} O(C_3H_6O)_{6.7}H \\ O(C_3H_6O)_{6.7}H \end{cases}$	74	2.8	56.0
Example 1-2	C_3H_6 $\begin{cases} O(C_3H_6O)_{14.0}COCH_3 \\ O(C_3H_6O)_{14.0}COCH_3 \end{cases}$	56	0.6	100
Comparative Example 1-2	C_3H_6 $\begin{cases} O(C_3H_6O)_{12.3}H \\ O(C_3H_6O)_{12.3}H \end{cases}$	40	1.5	101
Example 1-3	C_3H_5 $\begin{cases} O(C_3H_6O)_{6.5}COCH_3 \\ O(C_3H_6O)_{6.5}COCH_3 \\ O(C_3H_6O)_{6.5}COCH_3 \end{cases}$	67	1.0	101
Comparative Example 1-3	C_3H_5 $\begin{cases} O(C_3H_6O)_{5.2}H \\ O(C_3H_6O)_{5.2}H \\ O(C_3H_6O)_{5.2}H \end{cases}$	52	3.2	103
Example 1-4	$C_4H_9-O(C_3H_6O)_{21.7}COCH_3$	68	0.4	55.8
Comparative Example 1-4	$C_4H_9-O(C_3H_6O)_{19.1}H$	55	1.3	56.1
Example 1-5	C_3H_6 $\begin{cases} O(C_3H_6O)_8(C_2H_4O)_{6.5}COCH_3 \\ O(C_3H_6O)_8(C_2H_4O)_{6.5}COCH_3 \end{cases}$	51	1.2	102
Comparative Example 1-5	C_3H_6 $\begin{cases} O(C_3H_6O)_7(C_2H_4O)_6H \\ O(C_3H_6O)_7(C_2H_4O)_6H \end{cases}$	44	2.9	104

EXAMPLES 2-1 TO 2-7 AND COMPARATIVE EXAMPLE 2-1

Compounds (1) as identified in Tables 3 and 4 were tested for the solubility in R-134a and the stability.

A compound (1) and R-134a were sealed in a glass ampoule at a weight ratio of 30/70, and the solubility of the compound (1) in R-134a was determined by a visual observation of whether or not phase separation was observed. The results are shown in Table 1 together with the results of the Comparative Example.

Table 3

Compound (1): $R^2\text{-O-}(R^1O)_\ell\text{-}\underset{\underset{O}{\|}}{C}\text{-}OR^{11}$

	Compound (1)			Kinematic viscosity**	Solubility
	R^2	R^1	R^{11}		
Example 2-1	Butyl	Propylene	C_2H_5	32	Dissolved
Example 2-2	Butyl	Propylene	C_3H_7	35	Dissolved
Example 2-3	Butyl	Propylene	C_3H_7	62	Dissolved
Example 2-4	Butyl	Propylene	C_3H_7	102	Dissolved
Example 2-5	Butyl	Propylene	C_4H_9	35	Dissolved
Example 2-6	Butyl	Propylene	C_4H_9	56	Dissolved
Example 2-7	Butyl	Propylene	C_5H_{11}	55	Dissolved
Comparative Example 2-1	Suniso 4GS*			56	Insoluble

* Naphthene oil, manufactured by Nippon Sun Petroleum Corporation.

** $\times 10^{-6}\ m^2/s$ (cSt), at 40°C

A compound (1) and R-134a were sealed in a SUS316 pressure container in a weight ratio of 50/50 together with SS41 and Cu as representative metals and left to stand for 14 days at a high temperature of 175°C in a constant temperature tank. After the test, deterioration of the compound (1), R-134a and the metals was determined in comparison with the deterioration of the conventional combination of R-12 and Sniso 4GS. The results are shown in Table 4.

Table 4

	Compound (1)			Kinematic viscosity**	Stability
	R^2	R^1	R^{11}		
Example 2-1	Butyl	Propylene	C_2H_5	32	Good
Example 2-2	Butyl	Propylene	C_3H_7	35	Good
Example 2-3	Butyl	Propylene	C_3H_7	62	Good
Example 2-4	Butyl	Propylene	C_3H_7	102	Good
Example 2-5	Butyl	Propylene	C_4H_9	35	Good
Example 2-6	Butyl	Propylene	C_4H_9	56	Good
Example 2-7	Butyl	Propylene	C_5H_{11}	55	Good
Reference Example	Suniso 4GS*			56	Good

* Naphthene oil, manufactured by Nippon Sun Petroleum Corporation.

** $\times 10^{-6}$ m^2/s (cSt) at 40°C

EXAMPLES 3-1 TO 3-9 AND COMPARATIVE EXAMPLE 3-1

Compounds (2) as identified in Tables 5 and 6 were tested for the solubility in R-134a and the stability.

A compound (2) and R-134a were sealed in a glass ampoule in a weight ratio of 30/70, and the solubility of the compound (2) in R-134a was determined by a visual observation of whether or not phase separation was observed. The results are shown in Table 5 together with the Comparative Example.

Table 5

Compound (2): $R^2\text{-O-}(R^1O)_\ell\text{-}\underset{\underset{O}{\|}}{C}\text{-NHR}^{10}$

	Compound (2)			Kinematic viscosity**	Solubility
	R^2	R^1	R^{10}		
Example 3-1	Butyl	Propylene	CH_3	32	Dissolved
Example 3-2	Butyl	Propylene	CH_3	55	Dissolved
Example 3-3	Butyl	Propylene	CH_3	102	Dissolved
Example 3-4	Butyl	Propylene	C_2H_5	56	Dissolved
Example 3-5	Butyl	Propylene	$C_6H_5CH_2$	55	Dissolved
Example 3-6	Butyl	Propylene	$C_6H_5CH_2CH_2$	53	Dissolved
Example 3-7	Butyl	Propylene	C_6H_5	55	Dissolved
Example 3-8	Butyl	Propylene	$CH_3C_6H_4$	60	Dissolved
Example 3-9	Butyl	Propylene	$(CH_3)_2C_6H_3$	62	Dissolved
Comparative Example 3-1	Suniso 4GS*			56	Insoluble

* Naphthene oil, manufactured by Nippon Sun Petroleum Corporation.

** x $10^{-6}\ m^2/s$ (cSt) at 40°C

A compound (2) and R-134a were sealed in a SUS316 pressure container in a weight ratio of 50/50 together with SS41 and Cu as representative metals and left to stand for 14 days at a high temperature of 175°C in a constant temperature tank. After the test, deterioration of the compound (2), R-134a and the metals was ascertained in comparison with the deterioration of a conventional combination of R-12 and Sniso 4GS. The results are shown in Table 6.

Table 6

	Compound (2)			Kinematic viscosity**	Stability
	R^2	R^1	R^{10}		
Example 3-1	Butyl	Propylene	CH_3	32	Good
Example 3-2	Butyl	Propylene	CH_3	55	Good
Example 3-3	Butyl	Propylene	CH_3	102	Good
Example 3-4	Butyl	Propylene	C_2H_5	56	Good
Example 3-5	Butyl	Propylene	$C_6H_5CH_2$	55	Good
Example 3-6	Butyl	Propylene	$C_6H_5CH_2CH_2$	53	Good
Example 3-7	Butyl	Propylene	C_6H_5	55	Good
Example 3-8	Butyl	Propylene	$CH_3C_6H_4$	60	Good
Example 3-9	Butyl	Propylene	$(CH_3)_2C_6H_3$	62	Good
Reference Example	Suniso 4GS*			56	Good

* Naphthene oil, manufactured by Nippon Sun Petroleum Corporation.

** $\times 10^{-6}\ m^2/s$ (cSt) at 40°C

EXAMPLES 4-1 TO 4-7 AND COMPARATIVE EXAMPLE 4-1

Compounds (3) as identified in Tables 7 and 8 were tested for the solubility in R-134a and the stability.

A compound (3) and R-134a were sealed in a glass ampoule in a weight ratio of 30/70, and the solubility of the compound (3) in R-134a was determined by a visual observation of whether or not phase separation was observed. The results are shown in Table 7 together with the Comparative Example.

Table 7

Compound (3): $R^2\text{-O-}(R^1O)_\ell\text{-}R^3$

	Compound (3)			Kinematic viscosity**	Solubility
	R^2	R^1	R^3		
Example 4-1	Butyl	Propylene	CH_2CF_3	32	Dissolved
Example 4-2	Butyl	Propylene	CH_2CF_3	55	Dissolved
Example 4-3	Butyl	Propylene	$CH_2CF(CF_3)_2$	35	Dissolved
Example 4-4	Butyl	Propylene	$CH_2CF(CF_3)_2$	62	Dissolved
Example 4-5	Butyl	Propylene	$CH_2(CF_2)_6CF_3$	56	Dissolved
Example 4-6	Butyl	Propylene	$CH_2(CF_2)_6CF_3$	102	Dissolved
Example 4-7	Butyl	Propylene	$CH_2CH(CH_3)CHCl$	62	Dissolved
Comparative Example 4-1	Suniso 4GS*			56	Insoluble

* Naphthene oil, manufactured by Nippon Sun Petroleum Corporation.

** $\times 10^{-6}\ m^2/s$ (cSt) at 40°C

A compound (3) and R-134a were sealed in a SUS316 pressure container in a weight ratio of 50/50 together with SS41 and Cu as representative metals and left to stand for 14 days at a high temperature of 175°C in a constant temperature tank. After the test, deterioration of the compound (3), R-134a and the metals was ascertained in comparison with the deterioration of a conventional combination of R-12 and Sniso 4GS. The results are shown in Table 8.

Table 8

	Compound (3)			Kinematic viscosity**	Stability
	R^2	R^1	R^3		
Example 4-1	Butyl	Propylene	CH_2CF_3	32	Good
Example 4-2	Butyl	Propylene	CH_2CF_3	55	Good
Example 4-3	Butyl	Propylene	$CH_2CF(CF_3)_2$	35	Good
Example 4-4	Butyl	Propylene	$CH_2CF(CF_3)_2$	62	Good
Example 4-5	Butyl	Propylene	$CH_2(CF_2)_6CF_3$	56	Good
Example 4-6	Butyl	Propylene	$CH_2(CF_2)_6CF_3$	102	Good
Example 4-7	Butyl	Propylene	$CH_2CH(CH_3)CHCl$	62	Good
Reference Example	Suniso 4GS*			56	Good

* Naphthene oil, manufactured by Nippon Sun Petroleum Corporation.
** $\times 10^{-6}$ m^2/s (cSt) at 40°C

EXAMPLES 5-1 TO 5-6 AND COMPARATIVE EXAMPLES 5-1 TO 5-2

The structures of the oils used in Examples 5-1 to 5-5 and Comparative Examples 5-1, 5-2 and 5-6 and the test results for their compatibility with R-134a, hygroscopicity and kinematic viscosities at 40°C, are shown in Table 9.

Table 9

No.	Polyether	Upper critical solution temperature (°C) (Compati-bility with R-134a)	Kinematic viscosity at 40°C (cSt) x 10^{-6} m^2/s
Example 5-1	$C_4H_9O(C_3H_6O)_nCH_2\underset{O}{CH-CH_2}$	57	56
Example 5-2	$C_4H_9O(C_3H_6O)_m(C_2H_4O)_nCH_2-\underset{O}{CH-CH_2}$	58	54
Example 5-3	$C_3H_6\left\langle\begin{matrix}O(C_3H_6O)_mCH_2\underset{O}{CH-CH_2}\\ O(C_3H_6O)_nCH_2\underset{O}{CH-CH_2}\end{matrix}\right.$	60	52
Comparative Example 5-1	$C_4H_9O(C_3H_5O)_nH$	53	56
Example 5-4	$C_4H_9O(C_3H_6O)_nCH_2\underset{O}{CH-CH_2}$	80	32
Example 5-5	$C_4H_9O(C_3H_5O)_m(C_2H_4O)_nOCH_2\underset{O}{CH-CH_2}$	85	32
Comparative Example 5-6	$C_3H_6\left\langle\begin{matrix}O(C_3H_6O)_mCH_2\underset{O}{CH-CH_2}\\ O(C_3H_6O)_nCH_2\underset{O}{CH-CH_2}\end{matrix}\right.$	>100	2
Comparative Example 5-2	$C_4H_9O(C_3H_6O)_nH$	74	32

EXAMPLES 6-1 TO 6-5 AND COMPARATIVE EXAMPLES 6-1 TO 6-5

The structures of the oils used in Examples 6-1 to 6-5 and Comparative Examples 6-1 to 6-5 and the test results

for their compatibility with R-134a, hygroscopicity and kinematic viscosities at 40°C, are shown in Table 10.

Table 10

No.	Polyether	Upper critical solution temperature (°c) (Compatibility with R-134a)	Kinematic viscosity at 40°C (cSt) x 10^{-6} m^2/s
Example 6-1	$C_3H_6\begin{cases} O{+}C_3H_6O{+}_m C(=O)\text{-}CH_2OH \\ O{+}C_3H_6O{+}_m C(=O)\text{-}CH_2OH \end{cases}$	77	57
Comparative Example 6-1	$C_3H_6\begin{cases} O{+}C_3H_6O{+}_\ell H \\ O{+}C_3H_6O{+}_\ell H \end{cases}$	74	56
Example 6-2	$C_3H_6\begin{cases} O{+}C_3H_6O)_m\text{-}C(=O)\text{-}CH(CH_3)OH \\ O{+}C_3H_5O)_m\text{-}C(=O)\text{-}CH(CH_3)OH \end{cases}$	53	102
Comparative Example 6-2	$C_3H_6\begin{cases} O{+}C_3H_6O{+}_\ell H \\ O{+}C_3H_6O{+}_\ell H \end{cases}$	40	101
Example 6-3	$C_3H_5\begin{cases} O{+}C_3H_6O)_m\text{-}C(=O)\text{-}CH_2OH \\ O{+}C_3H_6O)_m\text{-}C(=O)\text{-}CH_2OH \\ O{+}C_3H_6O)_m\text{-}C(=O)\text{-}CH_2OH \end{cases}$	69	100
Comparative Example 6-3	$C_3H_5\begin{cases} O{+}C_3H_6O{+}_\ell H \\ O{+}C_3H_6O{+}_\ell H \\ O{+}C_3H_6O{+}_\ell H \end{cases}$	52	103

Table 10 (continued)

No.	Polyether	Upper critical solution temperature (°C) (Compatibility with R-134a)	Kinematic viscosity at 40°C (cSt) x 10^{-6} m^2/s
Example 6-4	$C_4H_9\text{-}O\text{-}(C_3H_6O)_m\text{-}\underset{\underset{O}{\Vert}}{C}\text{-}\underset{\underset{CH_3}{\vert}}{C}HOH$	71	54
Comparative Example 6-4	$C_4H_9\text{-}O\text{-}(C_3H_6O)_\ell H$	55	56
Example 6-5	$C_3H_6 \begin{cases} O\text{-}(C_3H_6O)_n(C_2H_4O)_m\text{-}\underset{\underset{O}{\Vert}}{C}\text{-}CH_2OH \\ O\text{-}(C_3H_6O)_n(C_2H_4O)_m\text{-}\underset{\underset{O}{\Vert}}{C}\text{-}CH_2OH \end{cases}$	50	101
Comparative Example 6-5	$C_3H_6 \begin{cases} O\text{-}(C_3H_6O)_\ell(C_2H_4O)_m\text{-}H \\ O\text{-}(C_3H_6O)_\ell(C_2H_4O)_m\text{-}H \end{cases}$	44	104

EXAMPLES 7-1 TO 7-5 AND COMPARATIVE EXAMPLES 7-1 TO 7-3

The structures of the oils used in Examples 7-1 to 7-5 and Comparative Examples 7-1 to 7-3 and the test results for their compatibility with R-134a, hygroscopicity and kinematic viscosities at 40°C, are shown in Table 11.

Table 11

No.	Polyether	Upper critical solution temperature (°C) (Compatibility with R-134a)	Kinematic viscosity at 40°C (cSt) x 10^{-6} m^2/s
Example 7-1	$H_3C-O-(C_3H_6O)_\ell-\underset{\|}{\overset{O}{C}}-C_4H_8-\underset{\|}{\overset{O}{C}}-(OC_3H_6)_\ell-O-CH_3$	82	55
Example 7-2	$H_9C_4-O-(C_3H_6O)_\ell-C(=O)-C_2H_4-C(=O)-(OC_3H_6)_\ell-O-C_4H_9$	79	56
Example 7-3	$H_3C-O-(C_3H_6O)_\ell-C(=O)-C_6H_4-C(=O)-(OC_3H_6)_\ell-O-CH_3$	80	57
Comparative Example 7-1	$C_3H_6\begin{cases} O-(C_3H_6O)_\ell H \\ O-(C_3H_6O)_\ell H \end{cases}$	74	56
Example 7-4	$H_3C-O-(C_2H_4O)_\ell-(C_3H_6O)_m-C(=O)-C_4H_8-C(=O)-(OC_3H_6)_m-(OC_2H_4)_\ell-O-CH_3$	93	33
Comparative Example 7-2	$C_4H_9-O-(C_3H_6O)_\ell H$	74	32
Example 7-5	$H_3C-O-(C_3H_6O)_\ell-C(=O)-C_4H_8-C(=O)-(OC_3H_6)_\ell-O-CH_3$	55	101
Comparative Example 7-3	$C_3H_5\begin{cases} O-(C_3H_6O)_\ell H \\ O-(C_3H_6O)_\ell H \end{cases}$	40	101

EXAMPLES 8-1 TO 8-5 AND COMPARATIVE EXAMPLES 8-1 TO 8-4

The structures of the oils used in Examples 8-1 to 8-5 and Comparative Examples 8-1 to 8-5 and the test results for their compatibility with R-134a, hygroscopicity and kinematic viscosities at 40°C, are shown in Table 12.

Table 12

No.	Polyether	Kinematic viscosity at 40°C (cSt) $\times 10^{-6}\,m^2/s$	Upper critical solution temperature (°C) (Compatibility with R-134a)	Weight increase (%) (Hygroscopicity)
Example 8-1	$C_3H_6 \left\langle \begin{matrix} O(C_3H_6O)_n\ SO_2CH_3 \\ O(C_3H_6O)_n\ SO_2CH_3 \end{matrix} \right.$	56.0	80	0.7
Comparative Example 8-1	$C_3H_6 \left\langle \begin{matrix} O(C_3H_6O)_m\ H \\ O(C_3H_6O)_m\ H \end{matrix} \right.$	56.0	74	2.8
Example 8-2	$C_3H_6 \left\langle \begin{matrix} O(C_3H_6O)_n\ SO_2C_2H_5 \\ O(C_3H_6O)_n\ SO_2C_2H_5 \end{matrix} \right.$	100	58	0.6
Comparative Example 8-2	$C_3H_6 \left\langle \begin{matrix} O(C_3H_6O)_m\ H \\ O(C_3H_6O)_m\ H \end{matrix} \right.$	101	40	1.5
Example 8-3	$C_3H_5 \left\langle \begin{matrix} O(C_3H_6O)_n\ SO_2C_6H_5 \\ O(C_3H_6O)_n\ SO_2C_6H_5 \\ O(C_3H_6O)_n\ SO_2C_6H_5 \end{matrix} \right.$	100	63	0.8
Comparative Example 8-3	$C_3H_5 \left\langle \begin{matrix} O(C_3H_6O)_m\ H \\ O(C_3H_6O)_m\ H \\ O(C_3H_6O)_m\ H \end{matrix} \right.$	103	52	3.2
Example 8-4	$C_4H_9\text{-}O\text{-}(C_3H_6O)_n\ SO_2\text{-}C_6H_4\text{-}CH_3$	56	63	0.4
Example 8-5	$C_3H_6 \left\langle \begin{matrix} O\text{-}(C_3H_6O)_m\text{-}(C_2H_4O)_n\ SO_2C_3H_7 \\ O\text{-}(C_3H_6O)_m\text{-}(C_2H_4O)_n\ SO_2C_3H_7 \end{matrix} \right.$	100	53	1.0
Comparative Example 8-4	$C_3H_6 \left\langle \begin{matrix} O\text{-}(C_3H_6O)_p\text{-}(C_2H_4O)_q\ H \\ O\text{-}(C_3H_6O)_p\text{-}(C_2H_4O)_q\ H \end{matrix} \right.$	104	44	2.9

EXAMPLES 9-1 TO 9-6 AND COMPARATIVE EXAMPLES 9-1 TO 9-6

The structures of the oils used in Examples 9-1 to 9-6 and Comparative Examples 9-1 to 9-6 and the test results for their compatibility with R-134a, hygroscopicity, viscosity indices and kinematic viscosities at 40°C, are shown in Table 13.

Table 13

No.	Polyether	Weight increase (%) (Hygroscopicity)	Viscosity index (VI)	Compatibility with R-134a	Kinematic viscosity (cSt/40°C) $\times 10^{-6}\ m^2/s$
Example 9-1	$C_3H_5 \begin{array}{l} O(C_3H_6O)_\ell-C_4H_9 \\ O(C_3H_6O)_\ell-C_4H_9 \end{array}$	0.9	162	Dissolved	59
Comparative Example 9-1	$C_3H_5 \begin{array}{l} O(C_3H_6O)_m-H \\ O(C_3H_6O)_m-H \end{array}$	2.8	135	Dissolved	56
Example 9-2	$C_3H_5 \begin{array}{l} O(C_3H_6O)_\ell-C_4H_9 \\ O(C_3H_6O)_\ell-C_4H_9 \end{array}$	0.7	196	Dissolved	101
Comparative Example 9-2	$C_3H_6 \begin{array}{l} O(C_3H_6O)_m-H \\ O(C_3H_6O)_m-H \end{array}$	1.5	170	Dissolved	101
Example 9-3	$C_3H_5 \begin{array}{l} O(C_3H_6O)_\ell-C_2H_5 \\ O(C_3H_6O)_\ell-C_2H_5 \\ O(C_3H_6O)_\ell-C_2H_5 \end{array}$	1.4	138	Dissolved	100
Comparative Example 9-3	$C_3H_5 \begin{array}{l} O(C_3H_6O)_m-H \\ O(C_3H_6O)_m-H \\ O(C_3H_6O)_m-H \end{array}$	3.2	118	Dissolved	103
Example 9-4	$C_4H_9-O(C_3H_6O)_\ell-CH_3$	0.5	211	Dissolved	57
Comparative Example 9-4	$C_4H_9-O(C_3H_6O)_m-H$	1.3	187	Dissolved	56
Example 9-5	$C_3H_6 \begin{array}{l} O(C_3H_6O)_\ell(C_2H_4O)_m-CH_3 \\ O(C_3H_6O)_\ell(C_2H_4O)_m-CH_3 \end{array}$	0.9	245	Dissolved	101
Comparative Example 9-5	$C_3H_6 \begin{array}{l} O(C_3H_6O)_n(C_2H_4O)_pH \\ O(C_3H_6O)_n(C_2H_4O)_pH \end{array}$	2.9	228	Dissolved	104
Comparative Example 9-6	Suniso 4SG	-	-	Insoluble	56
Example 9-6	$CH_3-O-(C_3H_6O)_n-CH_3$	0.7	214	Dissolved	55

Viscosity index:

The viscosity index is a value representing the temperature dependency of the viscosity of a lubricating oil. The larger the value, the smaller the change of the viscosity due to the temperature, and accordingly the better the lubricating properties.

Compatibility with R-134a:

An oil and R-134a are mixed in a weight ratio of 15:85 and sealed. The temperature is maintained at 25°C, and the solubility is visually observed.

EXAMPLES 10-1 TO 10-5 AND COMPARATIVE EXAMPLES 10-1 TO 10-6

The structures of the oils used in Examples 10-1 to 10-5 and Comparative Examples 10-1 to 10-6 and the test results for their compatibility with R-134a, hygroscopicity and kinematic viscosities at 40°C, are shown in Table 14.

Table 14

No.	Polyether	Upper critical solution temperature (°C) (Compatibility with R-134a)	Kinematic viscosity at 40°C (cSt) x 10^{-6} m^2/s
Example 10-1	C_3H_6 < $O\text{-}(C_3H_6O)_m\text{-}C(=O)\text{-}CF_3$ $O\text{-}(C_3H_6O)_m\text{-}C(=O)\text{-}CF_3$	78	55
Comparative Example 10-1	C_3H_6 < $O\text{-}(C_3H_5O)_\ell H$ $O\text{-}(C_3H_5O)_\ell H$	74	56
Example 10-2	C_3H_6 < $O\text{-}(C_3H_6O)_m\text{-}C(=O)\text{-}CCl_3$ $O\text{-}(C_3H_5O)_m\text{-}C(=O)\text{-}CCl_3$	58	101
Comparative Example 10-2	C_3H_6 < $O\text{-}(C_3H_6O)_\ell H$ $O\text{-}(C_3H_5O)_\ell H$	40	101
Example 10-3	C_3H_5 < $O\text{-}(C_3H_6O)_m\text{-}C(=O)\text{-}CF_3$ $O\text{-}(C_3H_6O)_m\text{-}C(=O)\text{-}CF_3$ $O\text{-}(C_3H_6O)_m\text{-}C(=O)\text{-}CF_3$	67	102
Comparative Example 10-3	C_3H_5 < $O\text{-}(C_3H_6O)_\ell H$ $O\text{-}(C_3H_6O)_\ell H$ $O\text{-}(C_3H_6O)_\ell H$	52	103

Table 14 (continued)

No.	Polyether	Upper critical solution temperature (°C) (Compatibility with R-134a)	Kinematic viscosity at 40°C (cSt) x 10^{-6} m²/s
Example 10-4	$C_4H_9\text{-}O\text{-}(C_3H_6O)_m\text{-}\underset{\underset{O}{\parallel}}{C}\text{-}CF_3$	61	57
Comparative Example 10-4	$C_4H_9\text{-}O\text{-}(C_3H_6O)_\ell H$	55	56
Example 10-5	$C_3H_6 \begin{cases} O\text{-}(C_3H_6O)_m(C_2H_4O)_m\text{-}\underset{\underset{O}{\parallel}}{C}\text{-}CF_3 \\ O\text{-}(C_3H_6O)_m(C_2H_4O)_m\text{-}\underset{\underset{O}{\parallel}}{C}\text{-}CF_3 \end{cases}$	52	100
Comparative Example 10-5	$C_3H_6 \begin{cases} O\text{-}(C_3H_6O)_\ell(C_2H_4O)_m\text{-}H \\ O\text{-}(C_3H_6O)_\ell(C_2H_4O)_m\text{-}H \end{cases}$	44	104
Example 10-6	$C_4H_9\text{-}O\text{-}(C_3H_6O)_m\text{-}\underset{\underset{O}{\parallel}}{C}\text{-}CH_2Cl$	41	100
Comparative Example 10-6	$C_4H_9\text{-}O\text{-}(C_3H_6O)_\ell\text{-}H$	12	101

EXAMPLES 11-1 TO 11-5 AND COMPARATIVE EXAMPLES 11-1 TO 11-2

The structures of the oils used in Examples 11-1 to 11-5 and Comparative Examples 11-1 to 11-2 and the test results for their compatibility with R-134a, hygroscopicity and kinematic viscosities at 40°C, are shown in Table 15.

Table 15

No.	Polyether	Upper critical solution temperature (°C) (Compatibility with R-134a)	Kinematic viscosity at 40°C (cSt) x 10^{-6} m^2/s
Example 11-1	$CF_3CH_2O(C_3H_5O)_\ell H$	120	32
Example 10-2	$CF_3CH_2O(C_3H_6O)_\ell H$	88	56
Example 11-3	$C_9F_{19}CH_2CH_2O(C_3H_5O)_\ell H$	36	102
Comparative Example 11-1	$C_{10}CH_{21}O(C_3H_6O)_mH$	13	100
Example 11-4	$C_3F_7CH_2O(C_3H_6O)_\ell(C_2H_4O)_mH$	84	54
Example 11-5	$(F_3C)_2CHCH_2O(C_3H_6O)_\ell(C_2H_4O)_mH$	89	55
Comparative Example 11-2	$(H_3C)_2CHCH_2O(C_3H_6O)_n(C_2H_4O)_pH$	61	56

The compositions of the present invention provide good compatibility of tetrafluoroethane and polyether oils, and they are capable of adequately providing functions such as the prevention of the friction, abrasion and seizing of sliding portions of e.g. compressors. Further, their hygroscopicity is low, and inclusion of moisture can be minimized, whereby a decrease of insulation resistance can be prevented, and the progress of corrosion of a metal such as a copper pipe by the moisture can be prevented.

Claims

1. A refrigeration composition, with functions of prevention of friction, abrasion and seizing of sliding portions, which comprises a tetrafluoroethane and at least one polyether selected from the group consisting of:

$$R^2-O-(R^1O)_\ell-R^3 \qquad (1)$$

$$X^1\begin{cases} O\text{-}(R^1O)_{\ell}\text{-}R^4 \\ O\text{-}(R^1O)_{m}\text{-}R^5 \end{cases} \qquad (2)$$

$$X^2\begin{cases} O\text{-}(R^1O)_{\ell}\text{-}R^6 \\ O\text{-}(R^1O)_{m}\text{-}R^7 \\ O\text{-}(R^1O)_{n}\text{-}R^8 \end{cases} \qquad (3)$$

wherein R^1 is an alkylene group, each of R^2, R^3, R^4, R^5, R^6, R^7 and R^8 which may be the same or different is a hydrogen atom, an alkyl group, a hydroxyalkyl group, an aralkyl group, an aryl group, an acyl group, a glycidyl group, $-SO_2R^9$,

$$-\underset{\underset{O}{\|}}{C}NHR^{10},$$

$$-\underset{\underset{O}{\|}}{C}OR^{11} \quad \text{or} \quad -Y^1\text{-}(OR^1)_p\text{-}OR^{12}$$

wherein R^1 is as defined above, each of R^9, R^{10}, R^{11} and R^{12} is an alkyl group, a hydroxyalkyl group, an aralkyl group or an aryl group, wherein all or a part of hydrogen atoms of said alkyl, aralkyl or aryl groups may be substituted by halogen atoms and Y^1 is a residue of a dicarboxylic compound having at least 3 carbon atoms, provided that at least one of R^2 and R^3 and at least one of R^4 and R^5 are not hydrogen atoms, and when R^2 is a hydrogen atom, an alkyl group for R^3 has 1 or 2 carbon atoms, and when R^3 is a hydrogen atom, an alkyl group for R^2 has 1 or 2 carbon atoms, ℓ, m, n and p which may be the same or different are integers which bring the kinematic viscosity of the compounds of the formulas (1) to (3) to a level of from 5×10^{-6} to 300×10^{-6} m^2/sec (5 to 300 cSt) at 40°C, X^1 is a residue obtained by removing hydroxyl groups from a dihydroxy compound or a dicarboxylic compound, and X^2 is a residue obtained by removing hydroxyl groups from a trihydroxy compound or a tricarboxylic compound.

2. The composition according to Claim 1, wherein the tetrafluoroethane is 1,1,1,2-tetrafluoroethane.

3. The composition according to Claim 1, wherein the weight ratio of the polyether to the tetrafluoroethane is from 1/99 to 99/1.

4. The composition according to Claim 1, which further contains at least one member. selected from the group consisting of a naphthene mineral oil, a paraffin mineral oil, an alkylbenzene synthetic oil, a poly-α-olefin synthetic oil and a fluorine-containing silicone oil.

5. The composition according to Claim 1, which further contains at least one stabilizer selected from the group consisting of a phosphite compound, a phosphine sulfide compound and a glycidyl ether compound.

6. The composition according to Claim 1, wherein R^1 in the formulas (1) to (3) is an ethylene group, a propylene group or a mixture of an ethylene group and a propylene group.

7. The composition according to Claim 1, wherein R^2 in the formula (1) is an alkyl group.

8. The composition according to Claim 1, wherein X^1 in the formula (2) is a propylene glycol residue.

9. The composition according to Claim 1, wherein X^2 in the formula (3) is a trimethylol propane residue.

10. The composition according to Claim 1, wherein R^2, R^3, R^4, R^5, R^6, R^7 and R^8 in the formulas (1) to (3) are the same or different acyl groups.

Patentansprüche

1. Kühlzusammensetzung mit der Funktion Reibung, Abrieb und Festfressen von verschiebbaren Teilen zu verhindern, die ein Tetrafluorethan und mindestens einen aus der Gruppe ausgewählten Polyether umfaßt, die aus:

$$R^2-O-(R^1O)_{\ell}-R^3 \qquad (1)$$

$$X^1 \left\langle \begin{array}{l} O-(R^1O)_{\ell}-R^4 \\ O-(R^1O)_{m}-R^5 \end{array} \right. \qquad (2)$$

$$X^2 - \left\{ \begin{array}{l} O-(R^1O)_{\ell}-R^6 \\ O-(R^1O)_{m}-R^7 \\ O-(R^1O)_{n}-R^8 \end{array} \right. \qquad (3)$$

besteht, worin R^1 eine Alkylengruppe ist, jedes R^2, R^3, R^4, R^5, R^6, R^7 und R^8, die gleich oder verschieden sein können, ein Wasserstoffatom, eine Alkylgruppe, eine Hydroxyalkylgruppe, eine Aralkylgruppe, eine Arylgruppe, eine Acylgruppe, ein Glycidylgruppe, $-SO_2R^9$,

$$-\underset{\displaystyle \overset{\|}{O}}{C}NHR^{10}, \qquad -\underset{\displaystyle \overset{\|}{O}}{C}OR^{11}$$

oder

$$-Y^1-(OR^1)_{p}-OR^{12}$$

ist, worin R^1 wie vorstehend definiert ist, jedes R^9, R^{10}, R^{11} und R^{12} eine Alkylgruppe, eine Hydroxyalkylgruppe, eine Aralkylgruppe oder eine Arylgruppe ist, worin alle oder ein Teil der Wasserstoffatome der Alkyl-, Aralkyl- oder Arylgruppen durch Halogenatome substituiert sein können und Y^1 ein Rest einer Dicarboxylverbindung mit mindestens 3 Kohlenstoffatomen ist, mit der Maßgabe, daß mindestens eine der Gruppen R^2 und R^3 und mindestens eine der Gruppen R^4 und R^5 keine Wasserstoffatome sind und wenn R^2 ein Wasserstoffatom ist, eine Alkylgruppe für R^3 ein oder zwei Kohlenstoffatome aufweist, und wenn R^3 ein Wasserstoffatom ist, eine Alkylgruppe für R^2 ein oder zwei Kohlenstoffatome aufweist, ℓ, m, n und p, die gleich oder verschieden sein können, ganze Zahlen sind,

die die kinematische Viskosität der Verbindungen der Formeln (1) bis (3) auf einen Wert von 5×10^{-6} bis 300×10^{-6} m^2/sec (5 bis 300 cSt) bei 40°C bringen, X^1 ein Rest ist, der durch Entfernen von Hydroxylgruppen von einer Dihydroxyverbindung oder einer Dicarboxylverbindung erhalten wird, und X^2 ein Rest ist, der durch Entfernen von Hydroxylgruppen von einer Trihydroxyverbindung oder einer Tricarboxylverbindung erhalten wird.

2. Zusammensetzung nach Anspruch 1, worin das Tetrafluorethan 1,1,1,2-Tetrafluorethan ist.

3. Zusammensetzung nach Anspruch 1, worin das Gewichtsverhältnis des Polyethers zu dem Tetrafluorethan von 1/99 bis 99/1 beträgt.

4. Zusammensetzung nach Anspruch 1, die außerdem mindestens ein aus der Gruppe ausgewähltes Mitglied umfaßt, die aus einem Naphthenmineralöl, einem Paraffinmineralöl, einem synthetischen Alkylbenzolöl, einem synthetischen Poly-α-Olefinöl und einem fluorhaltigen Siliconöl besteht.

5. Zusammensetzung nach Anspruch 1, die weiter mindestens einen aus der Gruppe ausgewählten Stabilisator enthält, die aus einer Phosphitverbindung, einer Phosphinsulfidverbindung und einer Glycidyletherverbindung besteht.

6. Zusammensetzung nach Anspruch 1, worin R^1 in den Formeln (1) bis (3) eine Ethylengruppe, eine Propylengruppe oder ein Gemisch aus einer Ethylengruppe und einer Propylengruppe ist.

7. Zusammensetzung nach Anspruch 1, worin R^2 in der Formel (1) eine Alkylgruppe ist.

8. Zusammensetzung nach Anspruch 1, worin X^1 in der Formel (2) ein Propylenglycolrest ist.

9. Zusammensetzung nach Anspruch 1, worin X^2 in der Formel (3) ein Trimethylolpropanrest ist.

10. Zusammensetzung nach Anspruch 1, worin R^2, R^3, R^4, R^5, R^6, R^7 und R^8 in den Formeln (1) bis (3) gleiche oder verschiedene Acylgruppen sind.

Revendications

1. Composition de réfrigération, avec des fonctions de prévention du frottement, de l'abrasion et du coincement de parties coulissantes, qui comprend un tétrafluoréthane et au moins un polyéther choisi dans le groupe constitué de :

$$R^2-O-(R^1O)_{\ell}-R^3 \qquad (1)$$

$$X^1 \begin{cases} O-(R^1O)_{\ell}-R^4 \\ O-(R^1O)_{m}-R^5 \end{cases} \qquad (2)$$

$$X^2 \begin{cases} O-(R^1O)_{\ell}-R^6 \\ O-(R^1O)_{m}-R^7 \\ O-(R^1O)_{n}-R^8 \end{cases} \qquad (3)$$

où R^1 est un groupe alkylène, chacun de R^2, R^3, R^4, R^5, R^6, R^7 et R^8, qui peuvent être les mêmes ou

différents, est un atome d'hydrogène, un groupe alkyle, un groupe hydroxyalkyle, un groupe aralkyle, un groupe aryle, un groupe acyle, un groupe glycidyle,

$$-\underset{\underset{O}{\|}}{C}NHR^{10}, \qquad -\underset{\underset{O}{\|}}{C}OR^{11}$$

ou

$$-Y^{1}\!\left(OR^{1}\right)_{p}\!-OR^{12}$$

où R^1 est tel que défini ci-dessus, chacun de R^9, R^{10}, R^{11} et R^{12} est un groupe alkyle, un groupe hydroxyalkyle, un groupe aralkyle ou un groupe aryle, où la totalité ou une partie des atomes d'hydrogène desdits groupes alkyle, aralkyle ou aryle peuvent être substitués par des atomes d'halogène, et Y^1 est un résidu d'un composé dicarboxylique ayant au moins 3 atomes de carbone, à la condition qu'au moins l'un parmi R^2 et R^3 et au moins l'un parmi R^4 et R^5 ne soient pas des atomes d'hydrogène, et, quand R^2 est un atome d'hydrogène, un groupe alkyle pour R^3 possède un ou deux atomes de carbone, et, quand R^3 est un atome d'hydrogène, un groupe alkyle pour R^2 possède un ou deux atomes de carbone, 1, m, n et p, qui peuvent être identiques ou différents, sont des entiers qui portent la viscosité cinématique des composés de formules (1) à (3) a une valeur de 5×10^{-6} à 300×10^{-6} m^2/s (de 5 à 300 cSt) à 40°c, X^1 est un résidu obtenu par élimination de groupes hydroxyle à partir d'un composé dihydroxylé ou d'un composé dicarboxylique, et X^2 est un résidu obtenu par élimination de groupes hydroxyle à partir d'un composé trihydroxylé ou d'un composé tricarboxylique.

2. Composition selon la revendication 1, dans laquelle le tétrafluoréthane est le 1,1,1,2-tétrafluoréthane.

3. Compositon selon la revendication 1, dans laquelle le rapport en poids du polyéther au tétrafluoréthane est de 1/99 à 99/1.

4. Composition selon la revendication 1, qui contient en outre au moins un élément choisi dans le groupe constitué d'une huile minérale naphténique, d'une huile minérale paraffinique, d'une huile synthétique à base d'un alkylbenzène, d'une huile synthétique à base d'une poly-α-oléfine et d'une huile de silicone fluorée.

5. Composition selon la revendication 1, qui contient en outre au moins un agent stabilisant sélectionné dans le groupe constitué d'un phosphite, d'un sulfure de phosphine et d'un glycidyléther.

6. Composition selon la revendication 1, dans laquelle R^1, dans les formules (1) à (3), est un groupe éthylène, un groupe propylène ou un mélange d'un groupe éthylène et d'un groupe propylène.

7. Composition selon la revendication 1, dans laquelle R^2, dans la formule (1), est un groupe alkyle.

8. Composition selon la revendication 1, dans laquelle X^1, dans la formule (2), est un résidu de propylèneglycol.

9. Composition selon la revendication 1, dans laquelle X^2, dans la formule (3), est un résidu de triméthylolpropane.

10. Composition selon la revendication 1, dans laquelle R^2, R^3, R^4, R^5, R^6,R^7 et R^8, dans les formules (1) à (3) sont des groupes acyle identiques ou différents.